Experimental investigation of the Mullins effect in swollen elastomers

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ABSTRACT: Natural rubber distinguishes itself by its particular mechanical properties. It has become an almost irreplaceable important component part in industrial applications such as vibration isolator, sealing system, flexible piping or structural bearing. During the service, these components are subjected to fluctuating mechanical loading. Under cyclic loading conditions, rubber exhibits strong inelastic responses such as stress-softening due to Mullins effect. It is believed that such inelastic response plays major role in determining the durability in service of rubber component. In engineering applications where the components are concurrently exposed to aggressive solvent, further material degradation in the form of swelling occurs. Thus, it is essential to investigate the effect of swelling on the stress-softening due to Mullins effect in rubber like materials for durability analysis. In this study, the Mullins effect in swollen carbon black-filled natural rubber under cyclic loading conditions is investigated. The swollen rubbers are obtained by immersing initially dry rubber in solvent at room temperature for various immersion durations. The stress-strain responses for both dry and swollen rubber are found qualitatively similar. However, the stress-softening in swollen rubbers are notably lower compared to that in the dry one. This work is later extended for future modelling purpose by adapting the concept of Continuum Damage Mechanics (CDM) [Chagnon, G., Verron,E., Gornet, L., Markmann, G., Charrier, P., 2004. On the relevance of Continuum Damage Mechanics as applied to the Mullins effect in elastomers. J. Mech. Phys. Sol. 52, 627-1650] and pseudo-elastic model [Ogden, R.W., Roxburgh, D.G., 1999. A pseudo-elastic model for the Mullins effect in filled rubber.Proc. R. Soc. A. 455, 2861-2877].

1 INTRODUCTION

Rubber acquires its own unique traits which enables it to be widely utilized under cyclic or fatigue loading conditions. Under cyclic loading, rubber exhibits inelastic responses such as hysteresis and stress softening. The viscoleasticity (Bergström and Boyce 1998) or viscoplasticity (Lion 1996) rubber characteristic may attribute to the hysteric behavior. The stress softening phenomena, or known prominently as the Mullins effect, can be related to a change of the mechanical properties after the material has been subjected to a deformation (Palmieri et al. 2009) and also defined as a non-neglectable loss of stiffness during the transition from the first cycle to the second one (Gracia et al. 2010).

Mullins effect greatly attracts the attention of many researchers in the twentieth century after it was successfully reported for the very first time of rubber vulcanizates by Bouasse and Carrière (1903). However, the corresponding stress-softening is referred to as the Mullins effect after Mullins (Mullins 1948). The Mullins effect is an important inelastic behavior which is said to appear in a stress-strain response when a lower consecutive stress is needed to achieve the same amount of stretch generated from the first loading phase (Diani et al. 2009).

Depending on its application, besides undergoing fluctuating loading, the rubber can be exposed to liquids such as water, seawater, organic solvents or even corrosive liquids. Upon exposure to such aggressive liquids, degradation of rubber in the form of swelling may occur (Haseeb et al. 2010). In fact, the properties of rubber deteriorates and hence affects the lifetime of the material. Yet, majority of the previous studies on Mullins effect and approaches in predicting the response of material was carried out for dry rubbers. Thus, the need to characterize the Mullins effect in swollen rubber becomes an imperative study. The recent phenomenological approach in modelling the mechanical response of rubber, which is, continuum damage mechanics (CDM) (Chagnon et al. 2004) and pseudo-elastic (Ogden and Roxburgh 1999) are considered in the present work to incorporate the swelling effect.

2 EXPERIMENTAL PROGRAM

The material investigated is a commercial grade of carbon black-filled natural rubber with 60 shore hardness and 25 wt% of carbon-black. The diabolo rubber specimens have a height, outer diameter, and wall thickness of 55 mm, 25 mm, and 6 mm respectively. The swollen rubber specimens are obtained by immersing dry specimens in diesel for 2 hours and 8 hours to achieve a 3% and 8% volume change respectively. No standard is followed regarding the choice of the specimens of immersion durations. When the specimens are subjected to mechanical testings, constant strain rate of 0.02 s^{-1} is prescribed to avoid any excessive increase of temperature in the specimen. The type of mechanical testing are elaborated as below:

1. Monotonic uniaxial tensile test. The specimen is subjected to an increasing monotonic tension load until it breaks.

2. Constant cyclic uniaxial tension test. The specimen is subjected to cyclic loading up to 100% engineering strain.

3. Strain increment cyclic uniaxial tension test. The specimen is subjected to a 50% engineering strain increment cyclic loading.

3 RESULTS AND DISCUSSION

3.1 Stress-stretch response

3.1.1 Test 1

The stress-stretch responses of dry and swollen rubbers subjected to simple monotonic tension loading up to fracture are shown in Figure 1. In this figure, no apparent difference is observed in the nature of stress-stretch behaviours between the dry and swollen rubbers. Nevertheless, the stress-stretch responses and strain at fracture of swollen rubbers are lower than the dry rubber since the presence of solvent in rubbers degrades their properties (Chai et al. 2013; Andriyana et al. 2012; Chai et al. 2011).

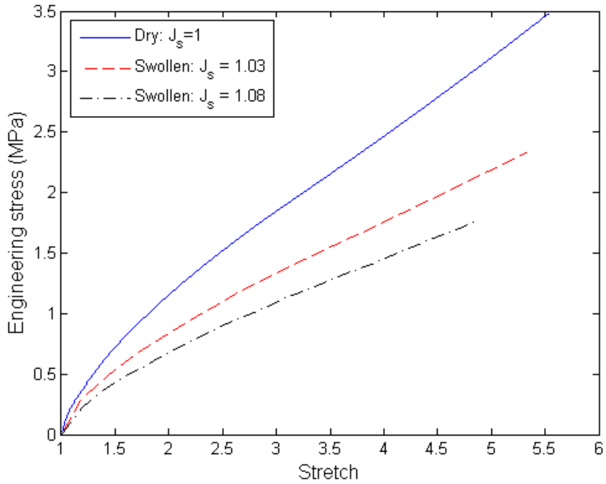

Figure 1. Stress-stretch curve of monotonic tension loading.

3.1.2 Test 2

The stress-stretch responses of dry and swollen rubber subjected to five cycles of cyclic uniaxial tension up to 100% engineering strain are presented in Figure 2. It is clearly shown that both dry and swollen rubbers exhibit strong inelastic behavior. However, the inelastic responses of stress-softening and hysteresis are lower for both swollen rubbers.

3.1.3 Test 3

The stress-stretch responses of dry and swollen rubber subjected to cyclic uniaxial tension loading with an increment of 50% engineering strain are shown in Figure 3. Generally, the stress-softening features are preserved for all three conditions at different swelling level. However, it is worth to note that there is no specific point that can be identified for the return of the reloading curve to the monotonous curve after being stretched beyond the maximum stretch previously applied.

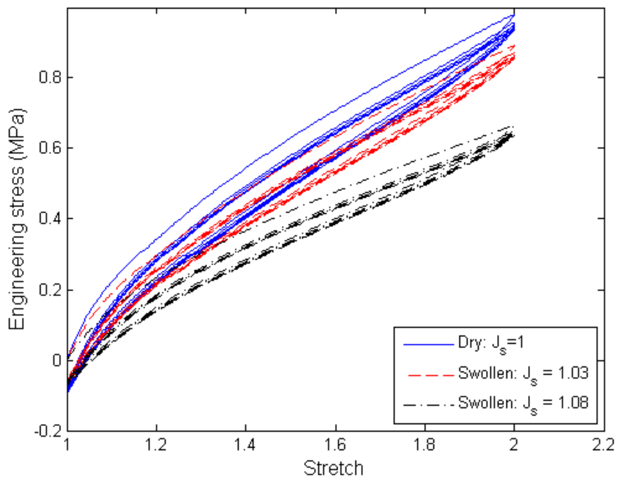

Figure 2. Stress-stretch curve of 5 cycles at maximum stretch of 2.

4 Continuum Damage Mechanics

For future modelling purpose, the concept of Continuum Damage Mechanics (CDM) is considered following the work of Chagnon et al. 2004 and is extended to incorporate the effect of swelling level J_s. Hence, the experimental results are shifted such that the unloading curves start from zero strain in order to separate the Mullins effect from viscoelasticity and permanent set. The treated experimental results are presented in Figure 4. In these figures, the solid line corresponds to the monotonic tensile and is referred to as the primary curve. The dashed lines are referred to as the secondary curves which correspond to the downloading path. According to Miehe 1995 and Chagnon et al. 2004 with assumption that Mullins effect depends exclusively on the maximum deformation experienced during the loading history, the damage variable d for dry rubber can be described by the following exponential-like equation

$$\bar{d}(\alpha_{\max}) = d_{\infty}\left[1 - \exp(\frac{-\alpha_{\max}}{\eta})\right] \tag{1}$$

$$\alpha_{\max} = \sqrt{\frac{I_{1\max}}{3}} - 1 \tag{2}$$

where $I_{1\max}$ is the maximum of the first invariant of the left Cauchy-Green strain tensor.

In order to investigate the explicit dependence of d and η on the swelling level J_s, the experimental values of damage variable d for both dry and swollen rubbers are plotted. The corresponding variable can be determined by considering the ratio between stresses at two successive secondary curves (Chagnon et al. 2004). By considering the treated experimental data of Figure 4, the example of corresponding ratios for dry and swollen rubbers is presented in Figure 5. As shown in this figure, the ratios are relatively constant for small strain (proportional zone A) and decrease

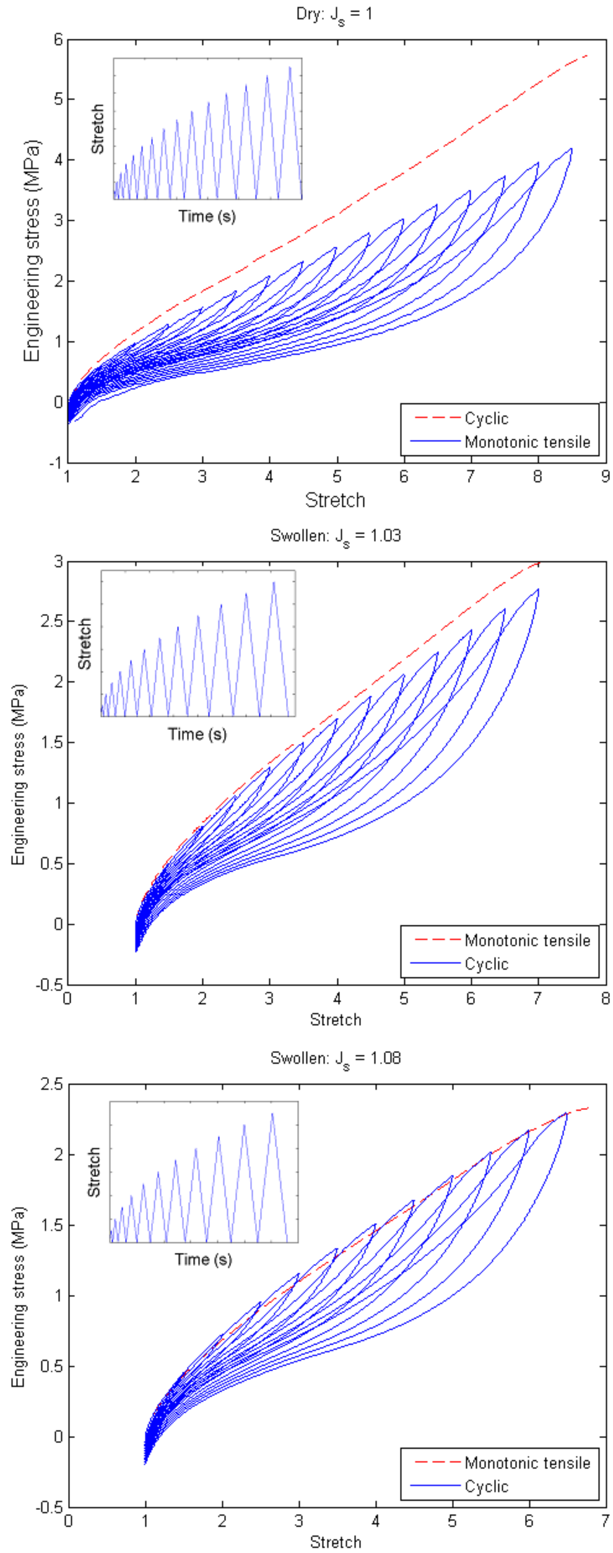

Figure 3. Stress-stretch curve of cyclic uniaxial tensile of dry and swollen natural rubbers. J_s stands for the change in volume.

for larger strain level (non-proportional zone B). By taking into consideration only the proportional zone, the evolution of damage variable as a function of maximum deformation state can be obtained for dry and swollen rubbers and it is presented in Figure 6. We observed that the damage decreases for an increasing swelling level. This observation is consistent with the

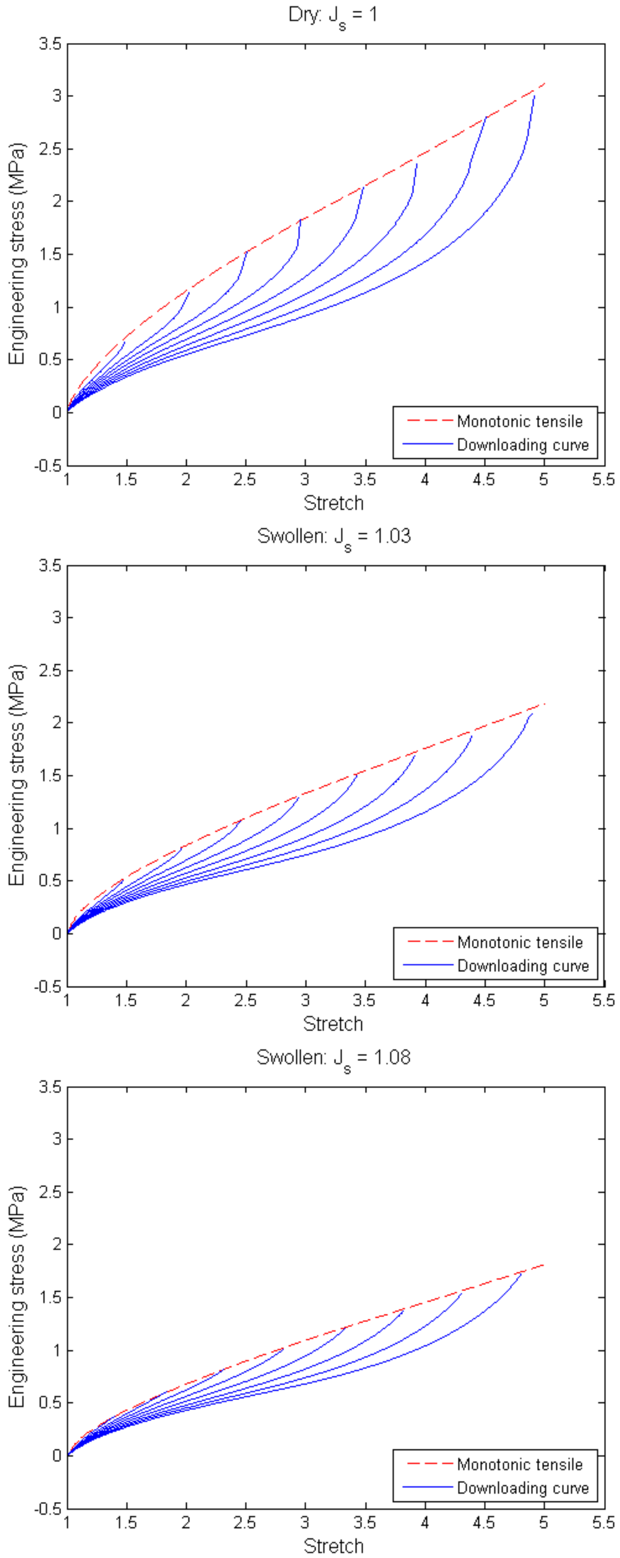

Figure 4. Treated experimental results.

previous observation that Mullins effect in swollen rubber is lower than that in dry one. In order to take into account the swelling level, Equation 1 can be phenomenologically extended by fitting the curves in Figure 6 with the following equations

$$d_\infty = d_{\infty 0} + a(J_s - 1) \tag{3}$$

$$\eta = \eta_0 + b(J_s - 1) \tag{4}$$

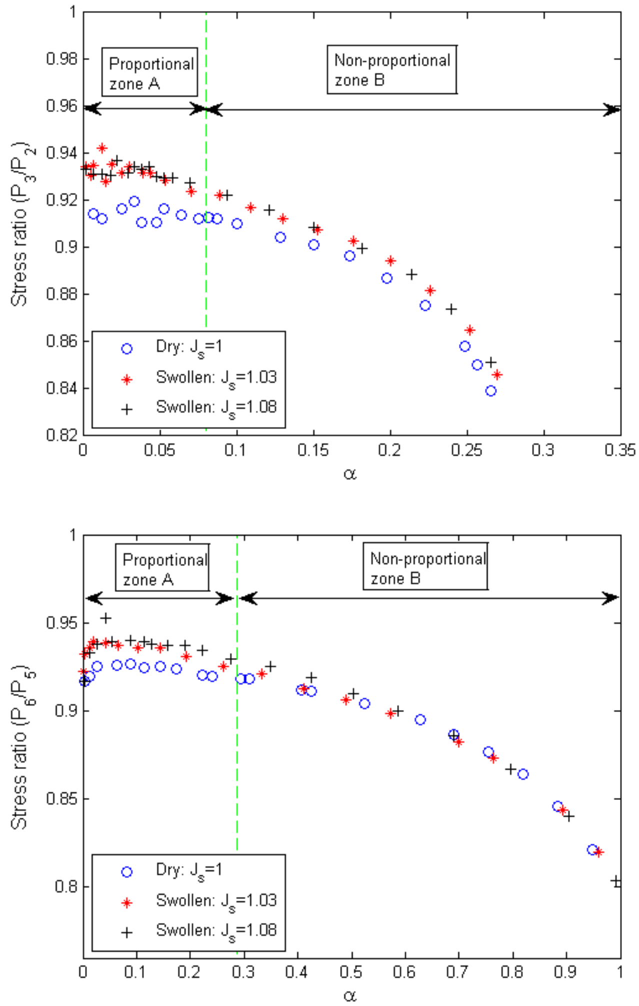

Figure 5. Example of ratio between two successive secondary curves: between the third and second secondary curves (top) and between the sixth and fifth secondary curves (bottom).

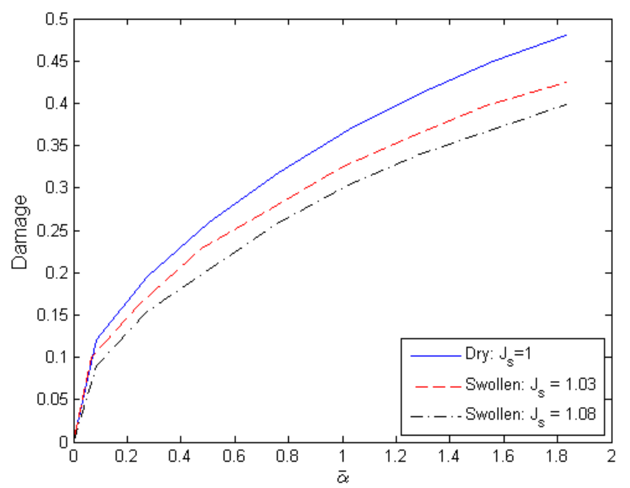

Figure 6. Damage curve for CDM.

where $d_{\infty 0}$ and η_0 are respectively the maximum possible damage and the damage saturation parameter of dry rubber. a<0 and b>0 are additional material parameters.

5 Pseudo-elastic

The pseudo-elastic model for Mullins effect (Ogden and Roxburgh 1999) is implemented to include the effect of swelling level J_s. With similar assumption in CDM on the maximum loading history, Ogden chose the strain energy density, W, as the measure of deformation with the damage variable given by:

$$\eta = 1 - \frac{1}{r}\text{erf}\left[\frac{1}{m}(W_{\text{max}} - W)\right] \tag{5}$$

In order to explore the data, we chose I_1 as the measure of deformation and the damage d can be described by the following equation

$$d = 1 - \frac{1}{r}\text{erf}\left[\frac{1}{m}(I_{1\text{max}} - I_1)\right] \tag{6}$$

The examples of evolution of damage d as a function of $I_{1\text{max}} - I_1$ are presented in Figure 7. Three secondary curves are considered: 3rd, 6th and 9th secondary curves. Recalling Equation 6, the parameter $1/r$ and $1/m$ correspond respectively to the maximum value of damage and the initial slope of damage curve. Moreover, by consulting Figure 7, it is clear that the maximum damage and the initial slope of the experimental damage curve depend strongly on the swelling level. In order to further investigate the explicit dependence of $1/r$ and $1/m$, the values of inverse initial slope (m) and inverse maximum damage (r) are plotted as a function of J_s - 1 and are presented in Figure 8. Based on the account of swelling level, it appears that r and m increase approximately linearly with the swelling level J_s. As the first step in modeling the Mullins effect in swollen rubbers, the following linear equations are considered

$$r = r_d + r_1(J_s - 1) \tag{7}$$

$$m = m_d + m_1(J_s - 1) \tag{8}$$

where r_d, r_1, m_d and m_1 are material parameters with positive values.

6 CONCLUSIONS

In the present work, the effect of stress-softening due to Mullins effect in swollen rubbers was investigated. Experimental works were carried out to see further the characteristic of Mullins effect in swollen rubbers and also the recovery of Mullins effect. It was observed that the features of Mullins effect were preserved in both dry and swollen natural rubbers. However, the amount of stress-softening in swollen rubbers was found lower than the one of dry rubber. Based on the experimental observations, perspectives toward the modeling of Mullins effect in swollen rubbers were drawn. Two models widely used in the literature were considered: continuum damage model and pseudo-elastic model. Subsequently, simple extension of the two previously mentioned models are proposed in order to account for swelling level.

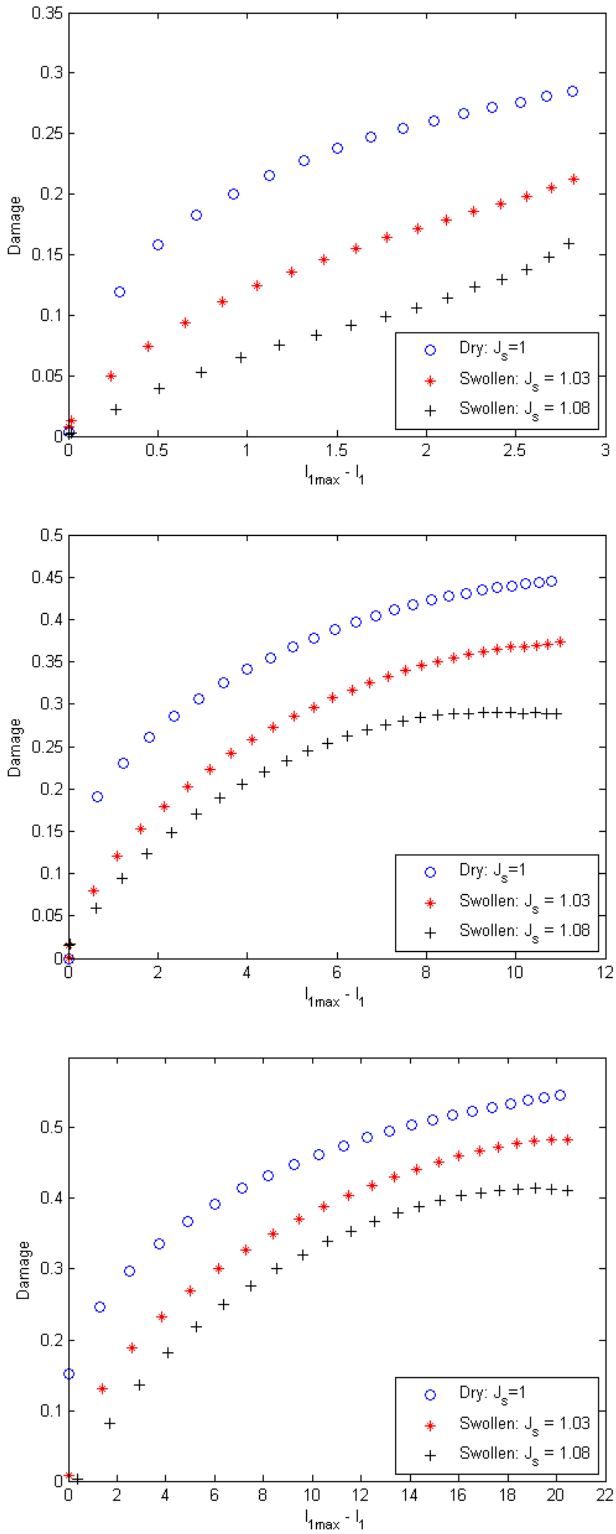

Figure 7. Damage evolution for different secondary curves. Damage evolution for different secondary curves.

7 ACKNOWLEDGEMENT

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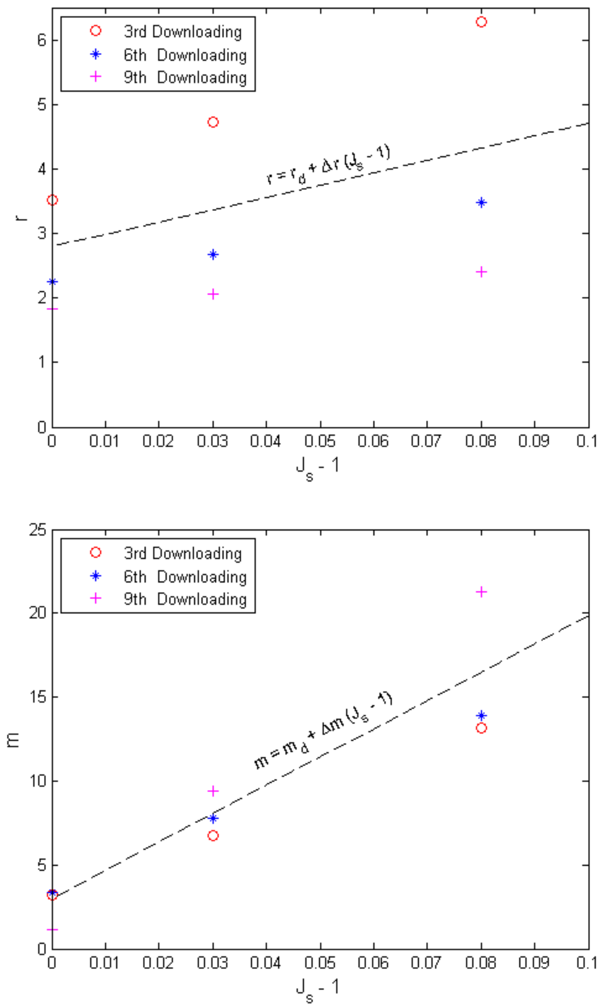

Figure 8. Plot of r(inverse of the maximum damage) and m(inverse of initial slope) as a function of swelling ratio.

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REFERENCES

Andriyana, A., A. B. Chai, E. Verron, and M. R. Johan (2012). Interaction between diffusion of palm biodiesel and large strain in rubber: Effect on stress-softening during cyclic loading. *Mech. Res. Commun 43*, 80–86.

Bergström, J. S. and M. C. Boyce (1998). Constitutive modeling of the large strain time-dependent behavior of elastomers. *J. Mech. Phys. Solids 46*(5), 931–954.

Chagnon, G., E. Verron, L. Gornet, G. Marckmann, and P. Charrier (2004). On the relevance of continuum damage mechanics as applied to the mullins effect in elastomers. *J. Mech. Phys. Solids 52*(7), 1627–1650.

Chai, A. B., A. Andriyana, E. Verron, and M. R. Johan (2013). Mechanical characteristics of swollen elastomers under cyclic loading. *Mater. Design 44*, 566–572.

Chai, A. B., A. Andriyana, E. Verron, M. R. Johan, and A. S. M. A. Haseeb (2011). Development of a compression test device for investigating interaction between diffusion of biodiesel and large deformation in rubber. *Polym. Test. 30*, 867–875.

Diani, J., B. Fayolle, and P. Gilormini (2009, March). A review on the Mullins effect. *Eur. Polym. J. 45*(3), 601–612.

Gracia, L., E. Liarte, J. Pelegay, and B. Calvo (2010). Finite element simulation of the hysteretic behaviour of an industrial rubber. application to design of rubber components. *Finite Elem. Anal. Des. 46*(4), 357–368.

Haseeb, A. S. M. A., H. H. Masjuki, C. T. Siang, and M. A. Fazal (2010). Compatibility of elastomers in palm biodiesel. *Renew. Energ. 35*(10), 2356–2361.

Lion, A. (1996). A constitutive model for carbon black filled rubber: experimental investigations and mathematical representation. *Continuum Mech. Therm. 8*(3), 153–169.

Miehe, C. (1995). Discontinuous and continuous damage evolution in ogden-type large-strain elastic materials. *Eur. J. Mech. A-Solid 14*(5), 697–720.

Mullins, L. (1948). Effect of stretching on the properties of rubber. *Rubber Chem. Technol. 21*(2), 281–300.

Ogden, R. and D. Roxburgh (1999). A pseudo–elastic model for the mullins effect in filled rubber. *Proc. R. Soc. London, Ser. A 455*(1988), 2861–2877.

Palmieri, G., M. Sasso, G. Chiappini, and D. Amodio (2009). Mullins effect characterization of elastomers by multi-axial cyclic tests and optical experimental methods. *Mech. Mater. 41*(9), 1059–1067.